

## Publication 1

## JAPANESE PATENT PUBLICATION (A)

(11) Publication number : 08-012333  
(43) Date of publication of application : 16.01.1996

(51) Int.CI. C01G 35/00  
C01G 33/00

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(30) Priority  
Priority number : 94 4422761 Priority date : 29.06.1994 Priority country : DE

(54) PRODUCTION OF TANTALUM HYDRATE AND/OR NIOBIUM OXIDE AND OBTAINED TANTALATE AND NIOBATE

(57) [ABSTRACT]

[OBJECT] Production of hydrated tantalum and/or niobium oxide and obtained tantalate and niobate

[CONFIGURATION] Production of spherical hydrated tantalum and/or niobium oxide or tantalum and/or niobium oxide by introducing an ammonium solution containing CO<sub>2</sub> into an acidic fluoride solution of Ta/Nb and controlling the pH to 7 or more and a metallic tantalate and/or a niobate obtained from said hydrate and oxide.

## [CLAIMS]

[Claim 1] A method for producing spherical hydrated tantalum and/or niobium oxide or tantalum and/or niobium oxide, characterized by introducing an ammonium solution containing  $\text{CO}_2$  into an acidic fluoride solution containing tantalum and/or niobium until the pH value of this solution becomes 7 or more.

[Claim 2] A method for producing a spherical tantalic acid and/or niobic acid metal, characterized by mixing the hydrated tantalum and/or niobium oxide produced by the method of claim 1 with a material selected from a group consisting of metallic oxides, hydroxides, and carbonates in corresponding stoichiometric amounts, then firing the obtained mixture.

## [DETAILED DESCRIPTION OF THE INVENTION]

## [0001]

[Background of the Invention] The present invention relates to a method for producing spherical hydrated tantalum and/or niobium oxide or tantalum and/or niobium oxide and a metallic tantalate and/or niobate obtained from them.

[0002] By performing hydrolysis of an organic tantalum compound by using the sol/gel method (Chem. Mater. 1991, 3, 335-339), spherical tantalum oxide can be obtained. However, this method is very expensive, so has shown absolutely no economical importance hitherto. No precipitation reaction using a fluoride or a chloride as the route known up to now gives a spherical product.

[0003] It is known from Japanese Patent Publication (A) No. 1-115820 that by adding a mixture of  $\text{NH}_3$  and  $(\text{NH}_4)_2\text{CO}_3$ , a hydroxide containing a low amount of fluorine is produced, but this is conditional on introducing an acidic solution of a test solution into the basic test solution and maintaining its basic range.  $\text{Ta}_2\text{O}_5$  is obtained in this way in various already known crystal forms, but this is not spherical. The sintering behavior and shrinkage behavior exhibited by such a product are inadequate. Accordingly, it is not suitable to use this as for example a starting materials for an electro-

ceramic component.

[0004] Accordingly, a main object of the present invention is to provide a method for producing spherical tantalum and/or niobium oxide not exhibiting described defects of the prior art.

[0005]

[Summary of the Invention] Surprising, it was discovered that spherical tantalum hydroxide or  $Ta_2O_5$  containing a low fluoride amount or spherical niobium hydroxide or  $Nb_2O_5$  containing a low fluoride amount is obtained when introducing a carbonic acid ammonium solution into an acidic fluoride solution containing tantalum and/or niobium until the pH value of this solution becomes 7 or more. This method is the main theme of the present invention. Preferably, by shifting this reaction from the acidic range to the basic range by adding a saturated carbonic acid ammonium solution into this transparent acidic metal fluoride solution, a precipitation reaction according to the present invention occurs. By doing this, a hydrated oxide which is easy to filter is obtained. It is very easy to wash this and, at the same time, the shape of principal particles of this is spherical. This spherical structure is held without damage even after the hydroxide is changed to an oxide by firing. This spherical structure is held without damage even when derivative is produced by using this hydroxide and reacting it with another metal oxide or metal carbonate. In this way, a mixed oxide or a tantalate and/or a niobate of a metal is produced while holding this spherical structure as it is without damage.

[0006] Especially economically, by introducing the  $CO_2$  released during this reaction into the  $NH_3$  water and reacting this with the  $NH_3$  used in the next precipitation step, the method according to the present invention can be executed.

[0007] Both of the oxide or hydrated oxide of tantalum and/or niobium available by the method according to the present invention and the tantalate and niobate produced from them are characterized in that the precipitation and filtering behavior exhibited by them is preferred, the

fluoride content is low, the particle size distribution is narrow, and the BET value is less than  $1\text{m}^2/\text{g}$ , so the surface area of the powder is small.

[0008]

[DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS] The following embodiments are intending to explain the present invention. The present invention is not limited by any aspect. In these embodiments, as described below, optical micrographs of FIGS. 1 to 5 taken at various powers are included as reference. Reference marks of 1 micrometer are attached to the figures.

[0009]

[Examples]

Example 1

A saturated carbonic acid ammonium solution was added to a solution containing tantalum fluoride (120 g of  $\text{Ta}_2\text{O}_5$  per liter) until the pH became 8.5. By introducing the  $\text{CO}_2$  released during this reaction into a 25%  $\text{NH}_3$  solution to cause the reaction, it was returned to the carbonic acid ammonium. The precipitated hydrated oxide was filtered on a suction filter, washed with a dilute  $\text{NH}_3$  solution or water by a well known method, dried, and then fired at  $850^\circ\text{C}$  for 2 hours. In the SEM micrograph, both of these dried hydrated Ta oxide and fired oxide had main spherical particles having diameters of 1  $\mu\text{m}$  (FIG. 1: 10,000 power at 20 kV).

[0010]

Spherical shape according to SEM (%)	>90
Tap density ( $\text{g}/\text{cm}^3$ )	2.2
Bulk density ( $\text{g}/\text{cubic inch}$ )	15.8
BET ( $\text{m}^2/\text{g}$ )*)	0.7

Particle size distribution ( $\mu\text{m}$ )

d90%	2.7
d50%	1.9
d10%	1.3
F in hydrated oxide (ppm)	300
F in sintered oxide (ppm)	<5

\*) Nitrogen one point method (measured by DIN 66 131)

## [0011] Example 2,

A 25% NH<sub>3</sub> solution was added to a solution containing niobium fluoride (about 120 g of Nb<sub>2</sub>O<sub>5</sub> per liter) until the pH became 6. Next, a saturated carbonic acid ammonium solution obtained by concentrating 25% of the NH<sub>3</sub> solution up to 5% by volume was added to control the pH value to 9. The precipitate of the hydrated oxide was washed by a diluted NH<sub>3</sub> solution and water on the suction filter by a well known method, dried, and then fired at 850°C for 2 hours. In the SEM micrograph, the main particles of the two were spherical particles having diameters of about 0.1 µm.

## [0012]

Spherical shape according to SEM (%)	>90
Tap density (g/cm <sup>3</sup> )	1.0
Bulk density (g/cubic inch)	6.9
BET (m <sup>2</sup> /g)	3
Particle size distribution (µm)	
d <sub>90%</sub>	3.8
d <sub>50%</sub>	1.7
d <sub>10%</sub>	1
F in hydrated oxide (ppm)	550

## Example 3

A 25% NH<sub>3</sub> solution was added to a solution containing niobium fluoride (about 120 g of Nb<sub>2</sub>O<sub>5</sub> per liter) until the pH became 6. Next, a saturated carbonic acid ammonium solution obtained by concentrating 25% of the NH<sub>3</sub> solution up to 5% by volume was added to control the pH to 9. The hydrated oxide precipitated after 2 days was washed by the diluted NH<sub>3</sub> solution and water on a suction filter by a well known method, dried, and then fired at 850°C for 2 hours.

[0013] The SEM micrograph shows that the main particles of both of these dried hydrated oxide and sintered oxide were spherical particles having diameter of about 0.1 µm (FIG; 2: 5000 power in 20 kv)

## [0014]

Spherical shape according to SEM (%)	>90
Tap density (g/cm <sup>3</sup> )	1.1

Bulk density (g/cubic inch)	10.3
BET (m <sup>2</sup> /g)	1.1
Particle size distribution (μm)	
d <sub>90%</sub>	8.4
d <sub>50%</sub>	5
d <sub>10%</sub>	3
F in hydrated oxide (ppm)	730

Example 4

25.54 g of Li<sub>2</sub>CO<sub>3</sub> (Li content: 18.7%) was added to 300 g of a moist tantalum oxide hydrate (Ta content: 41.5%) on a filter (filter-moist), then homogenized in a mixer for 1 hour. Next, this paste-like mixture was dried, then sintered at 1000°C for 2 hours.

[0015]

Lithium tantalate exhibiting a high phase purity was obtained. The main particles of this were spherical having a diameter of about 1 μm.

[0016]

Spherical shape according to SEM (%)	>90
Tap density (g/cm <sup>3</sup> )	1.6
Bulk density (g/cubic inch)	12
BET (m <sup>2</sup> /g)	0.81

Particle size distribution (μm)

d <sub>90%</sub>	9.8
d <sub>50%</sub>	5
d <sub>10%</sub>	2.8

Example 5

2000 g of a filter-moist tantalum oxide hydrate (Ta content: 41.5%), 255.2 g of a zinc hydroxycarbonate (Zn content: 59.8%), and 1381.4 g of barium carbonate were mixed together with 1500 ml of water and homogenized in a Thyssen-Henschel mixer for 30 minutes. This paste-like mixture was dried, and then fired at 1000°C for 2 hours.

[0017] A barium zinc tantalate exhibiting high phase purity was obtained. The main particles of this were spherical having a diameter of about 1 μm (FIG. 3: 10,000

power at 20 kV).

[0018]

Spherical shape according to SEM (%) >90

Tap density (g/cm<sup>3</sup>) 2

Bulk density (g/cubic inch) 16.5

BET (m<sup>2</sup>/g) 0.33

Particle size distribution (μm)

d<sub>90%</sub> 9.5

d<sub>50%</sub> 5.4

d<sub>10%</sub> 2.6

Example 6

3000 g of a tantalum oxide hydrate (Ta content: 74.19%) and 705.4 g of zinc hydroxycarbonate (Zn content: 57%) were mixed together with 3500 ml of water and homogenized in a Thyssen-Henschel mixer for 30 minutes. This paste-like mixture was dried, then fired at 1000°C for 2 hours.

[0019] The main particles of this obtained zinc tantalate exhibiting a high phase purity were spherical having a diameter of about 1 μm.

[0020]

Spherical shape according to SEM (%) >90

Tap density (g/cm<sup>3</sup>) 1.8

Bulk density (g/cubic inch) 14.0

BET (m<sup>2</sup>/g) 0.36

Particle size distribution (μm)

d<sub>90%</sub> 11.0

d<sub>50%</sub> 6.2

d<sub>10%</sub> 3.5

Example 7

3000 g of a tantalum oxide hydrate (Ta content: 74.19%) and 850.1 g of potassium carbonate (K content: 56.58%) were mixed together with 2500 ml of water and homogenized in a Thyssen-Henschel mixer for 30 minutes. This paste-like mixture was dried, then fired at 1000°C for 2 hours.

[0021] The main particles of this obtained potassium tantalate exhibiting a high phase purity were spherical having a diameter of about 1 μm.

## [0022]

Spherical shape according to SEM (%)	>90
Tap density (g/cm <sup>3</sup> )	1.9
Bulk density (g/cubic inch)	15.9
BET (m <sup>2</sup> /g)	0.31

## Particle size distribution (μm)

d90%	11.0
d50%	6.8
d10%	3.8

## Example 8

5000 g of a filter-moist niobium oxide hydrate (Nb content: 25%) and 497.1 g of lithium carbonate (Li content: 18.8%) were mixed together with 1000 ml of water and homogenized in a Thyssen-Henschel mixer for 30 minutes. This paste-like mixture was dried, then sintered at 850°C for 6 hours.

[0023] The main particles of this lithium niobate exhibiting a high phase purity were spherical having a diameter of about 1 μm.

## [0024]

Spherical shape according to SEM (%)	>90
Bulk density (g/cubic inch)	5.4
BET (m <sup>2</sup> /g)	1.5

## Particle size distribution (μm)

d90%	4.2
d50%	2.5
d10%	1.7

## Example 9

5000 g of a filter-moist niobium oxide hydrate (Nb content: 25%) and 929.7 g of potassium carbonate (K content: 56.58%) were mixed together with 1000 ml of water and homogenized in a Thyssen-Henschel mixer for 30 minutes. This paste-like mixture was dried, then fired at 850°C for 6 hours.

[0025] The main particles of this potassium niobate exhibiting a high phase purity were spherical having a diameter of about 1 μm.

[0026]

Spherical shape according to SEM (%) >90

Bulk density (g/cubic inch) 7.0

BET (m<sup>2</sup>/g) <2

Particle size distribution (μm)

d<sub>90%</sub> 3.5

d<sub>50%</sub> 2.0

d<sub>10%</sub> 1.2

Example 10

5000 g of a filter-moist niobium oxide hydrate (Nb content: 25%) and 290 g of magnesium hydroxycarbonate (Mg content: 57.58%) were mixed together with 2500 ml of water and homogenized in a Thyssen-Henschel mixer for 30 minutes. This paste-like mixture was dried, then fired at 850°C for 6 hours.

[0027] The main particles of this magnesium niobate exhibiting a high phase purity were spherical having a diameter of about 1 μm (FIG. 4: 5,000 power at 20 kV).

[0028]

Spherical shape according to SEM (%) >90

Bulk density (g/cubic inch) 6.4

BET (m<sup>2</sup>/g) 5.8

Particle size distribution (μm)

d<sub>90%</sub> 2.0

d<sub>50%</sub> 1.0

d<sub>10%</sub> 0.5

Example 11

2000 g of a filter-moist niobium oxide hydrate (Nb content: 25%) and 734.5 g of a nickel carbonate paste (Ni content: 21.5%) were mixed together with 500 ml of water and homogenized in a Thyssen-Henschel mixer for 30 minutes. This paste-like mixture was dried, then fired at 850°C for 6 hours. The main particles of this nickel niobate exhibiting a high phase purity were spherical having a diameter of about 1 μm (FIG. 5: 5,000 power at 20 kV).

[0029]

Spherical shape according to SEM (%)	>90
Bulk density (g/cubic inch),	6.7
BET (m <sup>2</sup> /g)	3.9
Particle size distribution (μm)	
d <sub>90%</sub>	2.5
d <sub>50%</sub>	1.3
d <sub>10%</sub>	0.6

Example 12

3000 g of a filter-moist niobium oxide hydrate (Nb content: 25%), 513.2 g of zinc hydroxycarbonate (Zn content: 54%), and 2389.6 g of barium carbonate (barium content: 69.59%) were mixed together with 3000 ml of water and homogenized in a Thyssen-Henschel mixer for 30 minutes. This paste-like mixture was dried, then fired at 850°C for 6 hours.

[0030] The main particles of this obtained barium zinc niobate exhibiting a high phase purity were spherical having a diameter of about 1 μm.

[0031]

Spherical shape according to SEM (%)	>90
Bulk density (g/cubic inch)	9.1
BET (m <sup>2</sup> /g)	<2
Particle size distribution (μm)	
d <sub>90%</sub>	4.0
d <sub>50%</sub>	2.2
d <sub>10%</sub>	1.4

The characteristic features and aspects of the present invention are as follows.

[0032] 1. A method for producing spherical hydrated tantalum and/or niobium oxide or tantalum and/or niobium oxide, characterized by introducing an ammonium solution containing CO<sub>2</sub> into an acidic fluoride solution containing tantalum and/or niobium until the pH value of this solution becomes 7 or more.

[0033] 2. A method as set forth in claim 1, characterized by introducing the CO<sub>2</sub> released during the reaction into NH<sub>3</sub> water and reacting it with this NH<sub>3</sub>, then

using this water in the next precipitation.

[0034] 3. Spherical hydrated tantalum and/or niobium oxide or tantalum and/or niobium oxide when produced by the method of claim 1 or claim 2.

[0035] 4. A method for producing spherical tantalic acid and/or niobic acid metal, characterized by mixing the hydrated tantalum and/or niobium oxide of claim 3 with a material selected from the group consisting of metallic oxides, hydroxides, and carbonates in corresponding stoichiometric amounts, then firing the obtained mixture.

[0036] 5. A spherical tantalic acid metal product produced by the method of claim 4.

[0037] 6. A spherical niobic acid metal product produced by the method of claim 4.

[0038] 7. A spherical tantalic acid/niobic acid metal product produced by the method of claim 4.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[FIG. 1] A scan type electron micrograph of particles of tantalum oxide obtained by Example 1.

[FIG. 2] A scan type electron micrograph of particles of niobium oxide obtained by Example 3.

[FIG. 3] A scan type electron micrograph of particles of barium zinc tantalate obtained by Example 5.

[FIG. 4] A scan type electron micrograph of particles of magnesium niobate obtained by Example 10.

[FIG. 5] A scan type electron micrograph of particles of nickel niobate obtained by Example 11.